

**COMMERCIAL-SCALE DEMONSTRATION OF THE  
LIQUID PHASE METHANOL (LPMEOH™) PROCESS**

**TECHNICAL PROGRESS REPORT NO. 23**

**For The Period**

**1 January - 31 March 2000**

**Prepared by**

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**and**

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**for the**

**Air Products Liquid Phase Conversion Company, L.P.**

**Prepared for the United States Department of Energy  
National Energy Technology Laboratory  
Under Cooperative Agreement No. DE-FC22-92PC90543**

**Patents cleared by Chicago on 23 June 2000.**

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## **Abstract**

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a \$213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. The LPMEOH™ Process Demonstration Unit was built at a site located at the Eastman chemicals-from-coal complex in Kingsport.

During the reporting period, the availability of the LPMEOH™ Demonstration Unit was 97.52%. A forced outage on 17 January 2000 lasted for 38 hours, and was caused by the failure of a localized section of the recirculation piping on a boiler feedwater pump. This represents the first LPMEOH™ Demonstration Unit forced outage since February 1999. The second forced outage, which occurred on 22 March 2000, was due to the failure of a control valve which regulates the flowrate of refined methanol from the distillation system. The plant was restarted after about 15 hours of downtime.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. After the addition of the final batch of catalyst, the total catalyst inventory was calculated to be 44,687 pounds.

A catalyst activation which was started on 26 January 2000 was aborted due to problems with the composition of the reducing gas. This reduction was initiated with 100 vol% carbon monoxide (CO) instead of the prescribed dilute CO stream (4 vol% CO in nitrogen). Changes in the control system and operating procedures have been instituted to prevent the reoccurrence of this event.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.64% per day was calculated for the period 31 December 1999 to 14 January 2000 (15 days). An overall deactivation rate of 0.72% per day was calculated for the period 29 February 2000 to 15 March 2000 (15 days). These deactivation results are greater than the baseline deactivation rate of 0.4% per day from the 4-month proof-of-concept run at the LaPorte Alternative Fuels Development Unit (AFDU) in 1988/89 (this run was performed at 250°C).

During most of the quarter, the flowrate of the primary syngas feed (Balanced Gas) was controlled between 680 and 800 KSCFH. During these operating periods, the reactor pressure was set at 710 psig and temperature was maintained at 235°C.

Two intervals of testing on CO-rich syngas were performed during the quarter. Upon restarting the LPMEOH™ Reactor on 23 February 2000 (after a syngas outage), the composition of the Balanced Gas stream was less than stoichiometric for the production of

methanol; this resulted in a ratio of hydrogen ( $H_2$ ) to CO in the reactor inlet of approximately 0.5. This period of operation on CO-rich syngas lasted about 24 hours.

On 21 March 2000, a syngas stream which contains primarily CO (CO Gas) was introduced with the Balanced Gas to achieve a 1:1  $H_2$ /CO reactor inlet feed composition. Reactor pressure was adjusted to 695 psig during this period of CO Gas addition to allow for proper control of the CO Gas. Operation at this condition continued until the forced outage on 22 March 2000. After the restart on 23 March 2000, CO-rich operation resumed; the test at a 1:1  $H_2$ /CO reactor inlet feed composition was maintained through the end of the reporting period. The operating period was not of sufficient length to calculate the rate of catalyst deactivation.

Process simulation work was performed in order to determine the operating procedures which could be used during a potential test of in-situ catalyst activation within the LPMEOH™ Reactor. Preliminary laboratory testing of the proposed procedure has begun and will continue into April of 2000 to fully evaluate the procedure.

Analyses of catalyst samples for changes in physical characteristics and levels of poisons have continued. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. Levels of arsenic are continuing to increase on catalyst samples, which confirms earlier observations that the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Plant and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas are no longer effective. Work is continuing to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur (another known catalyst poison) from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is continuing to increase in the most recent samples.

The performance of the gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, has met the expectations for pressure drop and reactor operation.

During the reporting period, a total of 5,951,853 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 53.5 million gallons of methanol has been produced. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No safety or environmental incidents were reported during this quarter.

During this quarter, planning, procurement, and test operations continued on two project sites selected for the off-site, product-use test program. Testing of stabilized methanol in the stationary gas turbine system at West Virginia University has been completed; indications are that the lubrication additive worked well during the final emissions testing. The initial phase of testing of both chemical-grade and stabilized methanol in the second generation methanol steam reforming apparatus at the University of Florida has been completed. The reformat produced with either fuel would be unacceptable for use in fuel cells due to the

relatively low methanol conversion rate at the high reformer operating temperature(96% vs. >99% minimum - excess methanol in the reformat will damage the fuel cell). In addition, tests with stabilized methanol showed the presence of oil at the reformer outlet, which would also be unacceptable. A search for a different reformer catalyst is underway.

During a Project Review Meeting on 12-13 January 2000, the preliminary results from the Fall 1999 design verification test of the Liquid Phase Dimethyl Ether (LPDME) Process at the LaPorte AFDU were presented. The results from the Design Verification Test Run were applied to a cost estimate for a commercial-scale LPDME plant. The sensitivity of the cost of production of DME to the life of the LPDME catalyst system was shown for the results from LaPorte (0.7% per day deactivation), as well as the impact of changes to the value for catalyst life on the process economics.

After discussing the results from the LPDME Design Verification Testing activities and the ongoing performance results from Kingsport, the meeting participants agreed that the available resources should be directed toward improving the catalyst performance for the LPMEOH™ Process during the remaining time within the operating program. The results of this economic analysis will be forwarded to the DOE's Liquid Fuels Program in order to provide direction to the ongoing catalyst development efforts. Work began to prepare the draft Topical Report on the results of the Design Verification Test operation at the LaPorte AFDU.

A formal request was made to DOE to approve a no-cost time extension to 31 March 2003 for the LPMEOH™ Demonstration Project. This extension is necessary to complete some of the key tests which were originally defined in the September 1996 Demonstration Test Plan, and to allow the opportunity to perform new tests of significant commercial interest (such as in-situ catalyst activation). Supporting information, including a project summary and chronology of events, was also prepared.

An abstract and paper entitled "Liquid Phase Methanol (LPMEOH™) Process Development" was accepted for presentation at Energex 2000 - The 8<sup>th</sup> International Energy Forum (23-28 July 2000). An abstract for the paper entitled "Catalyst and Process Development for Liquid Phase DME Synthesis" was submitted. This paper will be presented at 17<sup>th</sup> Annual International Pittsburgh Coal Conference (11-15 September 2000).

A proposed modification to the Environmental Monitoring Plan, which dealt with changes to the types of reports which will be produced by the Partnership, was approved by DOE.

Volume 1 - Public Design, of the Final Report for the LPMEOH™ Demonstration Project was issued during the reporting period.

Ninety-nine percent (99%) of the \$38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 March 2000. Fifty-five percent (55%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2000.

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## ACRONYMS AND DEFINITIONS

Acurex	-	Acurex Environmental Corporation (now ARCADIS Geraghty & Miller)
Air Products	-	Air Products and Chemicals, Inc.
AFDU	-	Alternative Fuels Development Unit - The "LaPorte PDU"
AFFTU	-	Alternative Fuels Field Trailer Unit
Balanced Gas	-	A syngas with a composition of hydrogen (H <sub>2</sub> ), carbon monoxide (CO), and carbon dioxide (CO <sub>2</sub> ) in stoichiometric balance for the production of methanol
Btu	-	British Thermal Unit
Carbon Monoxide Gas	-	A syngas containing primarily carbon monoxide (CO); also called CO Gas
Catalyst Activity	-	the rate at which the catalyst promotes the desired chemical reaction to proceed within the limitations of chemical equilibrium
Catalyst Age ( $\eta$ -eta)	-	the ratio of the rate constant at any point in time to the rate constant for a freshly reduced catalyst (as determined in the laboratory autoclave)
Catalyst Concentration	-	Synonym for Slurry Concentration
Catalyst Loading	-	Synonym for Slurry Concentration
CO Conversion	-	the percentage of CO consumed across the reactor
Crude Grade Methanol	-	Underflow from rectifier column (29C-20), defined as 80 wt% minimum purity; requires further distillation in existing Eastman equipment prior to use
DME	-	dimethyl ether
DOE	-	United States Department of Energy
DOE-NETL	-	The DOE's National Energy Technology Laboratory (Project Team)
DOE-HQ	-	The DOE's Headquarters - Coal Fuels and Industrial Systems (Project Team)
DTP	-	Demonstration Test Plan - The four-year Operating Plan for Phase 3, Task 2 Operation
DVT	-	Design Verification Testing
Eastman	-	Eastman Chemical Company
EIV	-	Environmental Information Volume
EMP	-	Environmental Monitoring Plan
EPRI	-	Electric Power Research Institute
FFV	-	flexible-fuel vehicle
Fresh Feed	-	sum of Balanced Gas, H <sub>2</sub> Gas, and CO Gas
Gas Holdup	-	the percentage of reactor volume up to the Gassed Slurry Height which is gas
Gassed Slurry Height	-	height of gassed slurry in the reactor
HAPs	-	Hazardous Air Pollutants
Hydrogen Gas	-	A syngas containing an excess of hydrogen (H <sub>2</sub> ) over the stoichiometric balance for the production of methanol; also called H <sub>2</sub> Gas
IGCC	-	Integrated Gasification Combined Cycle, a type of electric power generation plant
IGCC/OTM	-	An IGCC plant with a "Once-Thru Methanol" plant (the LPMEOH™ Process) added-on
Inlet Superficial Velocity	-	the ratio of the actual cubic feet of gas at the reactor inlet (calculated at the reactor temperature and pressure) to the reactor cross-sectional area (excluding the area contribution by the internal heat exchanger); typical units are feet per second
K	-	Sparger resistance coefficient (term used in calculation of pressure drop)
KSCFH	-	Thousand Standard Cubic Feet per Hour
LaPorte PDU	-	The DOE-owned experimental unit (PDU) located adjacent to Air Products' industrial gas facility at LaPorte, Texas, where the LPMEOH™ Process was successfully piloted
LPDME	-	Liquid Phase DME Process, for the production of DME as a mixed coproduct with methanol
LPMEOH™	-	Liquid Phase Methanol (the technology to be demonstrated)
M85	-	a fuel blend of 85 volume percent methanol and 15 volume percent unleaded gasoline
MeOH	-	methanol
Methanol Productivity	-	the gram-moles of methanol produced per hour per kilogram catalyst (on an oxide basis)
MW	-	molecular weight, pound per pound mole

## ACRONYMS AND DEFINITIONS (cont'd)

NEPA	-	National Environmental Policy Act
OSHA	-	Occupational Safety and Health Administration
$\rho$	-	density, pounds per cubic foot
Partnership	-	Air Products Liquid Phase Conversion Company, L.P.
PDU	-	Process Development Unit
PFD	-	Process Flow Diagram(s)
ppbv	-	parts per billion (volume basis)
ppmw	-	parts per million (weight basis)
Project	-	Production of Methanol/DME Using the LPMEOH™ Process at an Integrated Coal Gasification Facility
psi	-	pounds per square inch
psia	-	pounds per square inch (absolute)
psig	-	pounds per square inch (gauge)
P&ID	-	Piping and Instrumentation Diagram(s)
Raw Methanol	-	sum of Refined Grade Methanol and Crude Grade Methanol; represents total methanol which is produced after stabilization
Reactor Feed	-	sum of Fresh Feed and Recycle Gas
Reactor O-T-M Conversion	-	percentage of energy (on a lower heating value basis) in the Reactor Feed converted to methanol (Once-Through-Methanol basis)
Reactor Volumetric Productivity	-	the quantity of Raw Methanol produced (tons per day) per cubic foot of reactor volume up to the Gassed Slurry Level
Recycle Gas	-	the portion of unreacted syngas effluent from the reactor "recycled" as a feed gas
Refined Grade Methanol	-	Distilled methanol, defined as 99.8 wt% minimum purity; used directly in downstream Eastman processes
SCF	-	Standard Cubic Feet
SCFH	-	Standard Cubic Feet per Hour
Slurry Concentration	-	percentage of weight of slurry (solid plus liquid) which is catalyst (on an oxide basis)
Sl/hr-kg	-	Standard Liter(s) per Hour per Kilogram of Catalyst
Syngas	-	Abbreviation for Synthesis Gas
Syngas Utilization	-	defined as the number of standard cubic feet of Balanced Gas plus CO Gas to the LPMEOH™ Demonstration Unit required to produce one pound of Raw Methanol
Synthesis Gas	-	A gas containing primarily hydrogen (H <sub>2</sub> ) and carbon monoxide (CO), or mixtures of H <sub>2</sub> and CO; intended for "synthesis" in a reactor to form methanol and/or other hydrocarbons (synthesis gas may also contain CO <sub>2</sub> , water, and other gases)
Tie-in(s)	-	the interconnection(s) between the LPMEOH™ Process Demonstration Unit and the Eastman Facility
TPD	-	Ton(s) per Day
V	-	volumetric flowrate, thousand standard cubic feet per hour
VOC	-	volatile organic compound
vol%	-	volume %
WBS	-	Work Breakdown Structure
wt	-	weight



## **Executive Summary**

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a \$213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. The LPMEOH™ Process Demonstration Unit was designed, constructed, and is in operation at a site located at the Eastman chemicals-from-coal complex in Kingsport.

On 04 October 1994, Air Products and Eastman signed the agreements that would form the Partnership, secure the demonstration site, and provide the financial commitment and overall project management for the project. These partnership agreements became effective on 15 March 1995, when DOE authorized the commencement of Budget Period No. 2 (Modification No. A008 to the Cooperative Agreement). The Partnership has subcontracted with Air Products to provide the overall management of the project, and to act as the primary interface with DOE. As subcontractor to the Partnership, Air Products provided the engineering design, procurement, construction, and commissioning of the LPMEOH™ Process Demonstration Unit, and is providing the technical and engineering supervision needed to conduct the operational testing program required as part of the project. As subcontractor to Air Products, Eastman is responsible for operation of the LPMEOH™ Process Demonstration Unit, and for the interconnection and supply of syngas, utilities, product storage, and other needed services.

The project involves the operation of an 80,000 gallons per day (260 tons per day (TPD)) methanol unit utilizing coal-derived syngas from Eastman's integrated coal gasification facility. The new equipment consists of syngas feed preparation and compression facilities, the liquid phase reactor and auxiliaries, product distillation facilities, and utilities.

The technology to be demonstrated is the product of a cooperative development effort by Air Products and DOE in a program that started in 1981. Developed to enhance electric power generation using integrated gasification combined cycle (IGCC) technology, the LPMEOH™ Process is ideally suited for directly processing gases produced by modern day coal gasifiers. Originally tested at the Alternative Fuels Development Unit (AFDU), a small, DOE-owned experimental unit in LaPorte, Texas, the technology provides several improvements essential for the economic coproduction of methanol and electricity directly from gasified coal. This liquid phase process suspends fine catalyst particles in an inert liquid, forming a slurry. The slurry dissipates the heat of the chemical reaction away from the catalyst surface, protecting the catalyst and allowing the methanol synthesis reaction to proceed at higher rates.

At the Eastman chemicals-from-coal complex, the technology is integrated with existing coal gasifiers. A carefully developed test plan will allow operations at Eastman to simulate electricity demand load-following in coal-based IGCC facilities. The operations will also demonstrate the enhanced stability and heat dissipation of the conversion process, its reliable

on/off operation, and its ability to produce methanol as a clean liquid fuel without additional upgrading. An off-site, product-use test program will be conducted to demonstrate the suitability of the methanol product as a transportation fuel and as a fuel for stationary applications for small modular electric power generators for distributed power.

The operating test phase and off-site product-use test program will demonstrate the commercial viability of the LPMEOH™ Process and allow utilities to evaluate the application of this technology in the coproduction of methanol with electricity. A typical commercial-scale IGCC coproduction facility, for example, could be expected to generate 200 to 350 MW of electricity, and to also manufacture 45,000 to 300,000 gallons per day of methanol (150 to 1,000 TPD). A successful demonstration at Kingsport will show the ability of a local resource (coal) to be converted in a reliable (storable) and environmentally preferable way to provide the clean energy needs of local communities for electric power and transportation.

This project has also been performing design verification testing (DVT), including laboratory- and pilot-scale research and market verification studies, to evaluate whether to include a demonstration of the production of dimethyl ether (DME) as a mixed coproduct with methanol. DME has several commercial uses. In a storable blend with methanol, the mixture can be used as a peaking fuel in gasification-based electric power generating facilities, or as a diesel engine fuel. Blends of methanol and DME can be used as chemical feedstocks for synthesizing chemicals, including new oxygenated fuel additives.

The project was reinitiated in October of 1993, when DOE approved a site change to the Kingsport location. DOE conditionally approved the Continuation Application to Budget Period No. 2 (Design and Construction) in March of 1995 and formally approved it on 01 June 1995 (Modification No. M009). After approval, the project initiated Phase 1 - Design - activities. Phase 2 - Construction - activities were initiated in October of 1995. The project required review under the National Environmental Policy Act (NEPA) to move to the construction phase. DOE prepared an Environmental Assessment (DOE/EA-1029), and subsequently a Finding of No Significant Impact (FONSI) was issued on 30 June 1995. The Cooperative Agreement was modified (Modification No. A011) on 08 October 1996, authorizing the transition from Budget Period No. 2 (Design and Construction) to the final Budget Period (Commissioning, Start-up, and Operation). This modification provides the full \$213,700,000 of authorized funding, with 56.7% participant cost share and 43.3% DOE cost share.

During the reporting period, the availability of the LPMEOH™ Demonstration Unit was 97.52%. A forced outage on 17 January 2000 lasted for 38 hours, and was caused by the failure of a localized section of the recirculation piping on a boiler feedwater pump. During the next opportunity, a redesigned section of piping with increased distance from the orifice will be installed; in the interim, inspection of suspect areas of the existing piping system will be performed. This represents the first LPMEOH™ Demonstration Unit forced outage since February 1999.

The second forced outage, which occurred on 22 March 2000, was due to the failure of a control valve which regulates the flowrate of refined methanol from the distillation system. The plant was restarted after about 15 hours of downtime.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. A series of four withdrawals were conducted on 19 and 20 January 2000. This was followed by five catalyst additions which were activated and added between 22 January and 10 February 2000. After the addition of the fifth batch of catalyst, the total catalyst inventory was calculated to be 44,687 pounds.

A catalyst activation which was started on 26 January 2000 was aborted due to problems with the composition of the reducing gas. This reduction was initiated with 100 vol% carbon monoxide (CO) instead of the prescribed dilute CO stream (4 vol% CO in nitrogen (N<sub>2</sub>)). Changes in the control system and operating procedures have been instituted to prevent the reoccurrence of this event.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.64% per day was calculated for the period 31 December 1999 to 14 January 2000 (15 days). An overall deactivation rate of 0.72% per day was calculated for the period 29 February 2000 to 15 March 2000 (15 days). These deactivation results are greater than the baseline deactivation rate of 0.4% per day from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (this run was performed at 250°C).

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On 21 March 2000, a syngas stream which contains primarily CO (CO Gas) was introduced with the Balanced Gas to achieve a 1:1 H<sub>2</sub>/CO reactor inlet feed composition. Reactor pressure was adjusted to 695 psig during this period of CO Gas addition to allow for proper control of the CO Gas. Approximately 40 KSCFH of CO Gas was introduced with approximately 600 KSCFH of Balanced Gas for this CO-rich feed case. Operation at this condition continued until the forced outage on 22 March 2000. After the restart on 23 March 2000, CO-rich operation resumed; the test at a 1:1 H<sub>2</sub>/CO reactor inlet feed composition was maintained through the end of the reporting period. The catalyst performance met expectations for the quantity of methanol which was produced at these conditions; however, the operating period was not of sufficient length to calculate the rate of catalyst deactivation.

Repairs to two transmitters in the oil addition circuit were made during the period from 11 February to 14 February 2000; during these interruptions, the expanded slurry height reached a minimum value of less than 50 feet (or 90% of design). The expanded slurry level was increased after completion of repairs on 15 February 2000. No impact to the system hydrodynamics or operation was observed.

Process simulation work was performed in order to determine the operating procedures which could be used during a potential test of in-situ catalyst activation within the LPMEOH™ Reactor. A protocol for testing the potential in-situ catalyst activation conditions in the laboratory autoclave was developed and formalized. Preliminary laboratory testing has begun and will continue into April of 2000 to fully evaluate the procedure.

Analyses of catalyst samples for changes in physical characteristics and levels of poisons have continued. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. Levels of arsenic are continuing to increase on catalyst samples, which confirms earlier observations that the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Plant and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas are no longer effective. Work is continuing to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur (another known catalyst poison) from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is continuing to increase in the most recent samples.

The performance of the gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The performance to date has met the design expectations for pressure drop and reactor operation.

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completed. Both fuels provide similar conversion rates and selectivities; however, the reformat produced with either fuel would be unacceptable for use in fuel cells due to the relatively low methanol conversion rate at the high reformer operating temperature (96% vs. >99% minimum - excess methanol in the reformat will damage the fuel cell). In addition, tests with stabilized methanol showed the presence of oil at the reformer outlet, which would also be unacceptable. A search for a different reformer catalyst is underway, and techniques to filter the oil from the stabilized methanol are being considered.

During a Project Review Meeting on 12-13 January 2000, the preliminary results from the Fall 1999 design verification test of the Liquid Phase Dimethyl Ether (LPDME) Process at the LaPorte AFDU were presented. The earlier results from the laboratory work had indicated that the targets for catalyst productivity and life can be met at lower selectivity to DME. The results from the Design Verification Test Run were applied to a cost estimate for a commercial-scale LPDME plant. The target DME cost (\$7 to \$8 per million Btu's) can likely be achieved at larger plant sizes by extrapolating the costs to the 1,100 short tons-per-day production rates. The sensitivity of the cost of production of DME to the life of the LPDME catalyst system was shown for the results from LaPorte (0.7% per day deactivation), as well as the impact of changes to the value for catalyst life on the process economics.

After discussing the results from the LPDME Design Verification Testing activities and the ongoing performance results from Kingsport, the meeting participants agreed that the available resources should be directed toward improving the catalyst performance for the LPMEOH™ Process during the remaining time within the operating program. The results of this economic analysis will be forwarded to the DOE's Liquid Fuels Program in order to provide direction to the ongoing catalyst development efforts.

Work began to prepare the draft Topical Report on the results of the Design Verification Test operation at the LaPorte AFDU; this report, which will be published under the LPMEOH™ Demonstration Project; is expected to be released by 31 July 2000.

A formal request was made to DOE to approve a no-cost time extension to 31 March 2003 for the LPMEOH™ Demonstration Project. This extension is necessary to complete some of the key tests which were originally defined in the September 1996 Demonstration Test Plan, and to allow the opportunity to perform new tests of significant commercial interest (such as in-situ catalyst activation). Supporting information, including a project summary and chronology of events, was also prepared.

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Ninety-nine percent (99%) of the \$38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 March 2000. Fifty-five percent (55%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2000.

## **A. Introduction**

The Liquid Phase Methanol (LPMEOH™) demonstration project at Kingsport, Tennessee, is a \$213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L. P. (the Partnership). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. A demonstration unit producing 80,000 gallons per day (260 TPD) of methanol was designed, constructed, and is operating at a site located at the Eastman chemicals-from-coal complex in Kingsport. The Partnership will own and operate the facility for the four-year demonstration period.

This project is sponsored under the DOE's Clean Coal Technology Program, and its primary objective is to “demonstrate the production of methanol using the LPMEOH™ Process in conjunction with an integrated coal gasification facility.” The project will also demonstrate the suitability of the methanol produced for use as a chemical feedstock or as a low-sulfur dioxide, low-nitrogen oxides alternative fuel in stationary and transportation applications. The project may also demonstrate the production of dimethyl ether (DME) as a mixed coproduct with methanol, if laboratory- and pilot-scale research and market verification studies show promising results. If implemented, the DME would be produced during the last six months of the four-year demonstration period.

The LPMEOH™ Process is the product of a cooperative development effort by Air Products and the DOE in a program that started in 1981. It was successfully piloted at a 10-TPD rate in the DOE-owned experimental unit at Air Products' LaPorte, Texas, site. This demonstration project is the culmination of that extensive cooperative development effort.

## **B. Project Description**

The demonstration unit, which occupies an area of 0.6 acre, is integrated into the existing 4,000-acre Eastman complex located in Kingsport, Tennessee. The Eastman complex employs approximately 8,600 people. In 1983, Eastman constructed a coal gasification facility utilizing Texaco technology. The synthesis gas (syngas) generated by this gasification facility is used to produce carbon monoxide and methanol. Both of these products are used to produce methyl acetate and ultimately cellulose acetate and acetic acid. The availability of this highly reliable coal gasification facility was the major factor in selecting this location for the LPMEOH™ Process Demonstration. Three different feed gas streams (hydrogen gas or H<sub>2</sub> Gas, carbon monoxide gas or CO Gas, and the primary syngas feed known as Balanced Gas) are diverted from existing operations to the LPMEOH™

Demonstration Unit, thus providing the range of coal-derived syngas ratios (hydrogen to carbon monoxide) needed to meet the technical objectives of the demonstration project.

For descriptive purposes and for design and construction scheduling, the project has been divided into four major process areas with their associated equipment:

- *Reaction Area* - Syngas preparation and methanol synthesis reaction equipment.
- *Purification Area* - Product separation and purification equipment.
- *Catalyst Preparation Area* - Catalyst and slurry preparation and disposal equipment.
- *Storage/Utility Area* - Methanol product, slurry, and oil storage equipment.

The physical appearance of this facility closely resembles the adjacent Eastman process plants, including process equipment in steel structures.

- *Reaction Area*

The reaction area includes feed gas compressors, catalyst guard beds, the reactor, a steam drum, separators, heat exchangers, and pumps. The equipment is supported by a matrix of structural steel. The most salient feature is the reactor, since with supports, it is approximately 84-feet tall.

- *Purification Area*

The purification area features two distillation columns with supports; one is approximately 82-feet tall, and the other 97-feet tall. These vessels resemble the columns of the surrounding process areas. In addition to the columns, this area includes the associated reboilers, condensers, air coolers, separators, and pumps.

- *Catalyst Preparation Area*

The catalyst preparation area consists of a building with a roof and partial walls, in which the catalyst preparation vessels, slurry handling equipment, and spent slurry disposal equipment are housed. In addition, a hot oil utility system is included in the area.

- *Storage/Utility Area*

The storage/utility area includes two diked lot-tanks for methanol, two tanks for oil storage, a slurry holdup tank, a trailer loading/unloading area, and an underground oil/water separator. A vent stack for safety relief devices is located in this area.

## **C. Process Description**

The LPMEOH™ Demonstration Unit is integrated with Eastman's coal gasification facility. A simplified process flow diagram is included in Appendix A. Syngas is introduced into the slurry reactor, which contains a slurry of liquid mineral oil with suspended solid particles of catalyst. The syngas dissolves through the mineral oil, contacts the catalyst, and reacts to form methanol. The heat of reaction is absorbed by the slurry and is removed from the slurry by steam coils. The methanol vapor leaves the reactor, is condensed to a liquid, sent to the distillation columns for removal of higher alcohols, water, and other impurities, and is then stored in the day tanks for sampling before being sent to Eastman's methanol storage. Most of the unreacted syngas is recycled back to the reactor with the syngas recycle compressor, improving cycle efficiency. The methanol will be used for downstream feedstocks and in off-site, product-use testing to determine its suitability as a transportation fuel and as a fuel for stationary applications in the power industry.

## **D. Results and Discussion**

The project status is reported by task, covering those areas in which activity took place during the reporting period. Major accomplishments during this period are as follows:

### ***D.1 Off-Site Testing (Product-Use Demonstration)***

#### **Discussion**

The product-use test program, developed in 1992 to support the demonstration at the original Cool Water Gasification Facility site, became outdated due in large part to changes within the power and chemical industries. This original product test program under-represented new utility dispersed electric power developments, and possibly new mobile transport engine developments. The updated product-use test program attempts for broader market applications and for commercial fuels comparisons. The objective of the product-use test program is to demonstrate commercial market applications for the “as produced” methanol as a replacement fuel and as a fuel supplement. Fuel economics will be evaluated for the “as produced” methanol for use in municipal, industrial, and utility applications and as fuel supplements for gasoline, diesel, and natural gas. These fuel evaluations will be based on the U.S. energy market needs projected during the 1998 to 2018 time period when the LPMEOH™ technology is expected to be commercialized.

The product-use test program has been developed to enhance the early commercial acceptance of central clean coal technology processing facilities, coproducing electricity and methanol to meet the needs of the local community. One of the advantages of the LPMEOH™ Process for coproduction from coal-derived syngas is that the as-produced, stabilized (degassed) methanol product is of unusually high quality (e.g. less than 1 wt% water) which may be suitable for the premium fuel applications. When compared to conventional methanol synthesis processes, cost savings (10 to 15%) of several cents per gallon of methanol can be achieved in coproduction facilities, if the suitability of the stabilized product as a fuel can be demonstrated. The applications (for example, as a



hydrogen source for fuel cells, and as a clean transportable, storable fuel for dispersed power) will require testing of the product to confirm its suitability. Chemical feedstock applications will also be tested as warranted.

A limited quantity (up to 400,000 gallons) of the methanol product as produced from the demonstration unit is being made available for product-use tests. Product-use tests are targeted for an approximate 18 to 30-month period, and commenced during the first year of demonstration operations. An initial inventory of approximately 12,000 gallons of stabilized methanol was produced at LPMEOH™ Demonstration Unit in February of 1998 to supply the needs of the product-use test program; due to the pre-1998 timing for certain tests, methanol was shipped from the inventory held at the LaPorte AFDU. Air Products, ARCADIS Geraghty & Miller, and the DOE have worked together to select the projects to be included in the off-site, product-use test program.

#### Activity during this quarter

During an evaluation period, eight sites involving a variety of product-use tests were selected to participate in this task. In a letter to the DOE dated 31 July 1997, Air Products formally recommended that seven of the eight projects had been defined in sufficient detail so that final planning and implementation should begin. DOE accepted Air Products' recommendation to proceed with the seven projects in August of 1997. The sites and project titles are listed in Appendix B-1. The eighth project, which involved the testing of a water/naphtha/methanol emulsion as a transportation fuel, was removed from the Product-Use Test Program during a review meeting between DOE, Air Products, and ARCADIS Geraghty & Miller.

All of the remaining product-use test projects are at varying phases of project planning, equipment procurement, and execution; two projects have been completed. Methanol produced from carbon monoxide (CO)-rich syngas at the LaPorte AFDU has been shipped to three of the project sites. Appendices B-2 and B-3 contain summary reports from the approved active projects. Highlights from these reports include:

ARCADIS Geraghty & Miller Flexible-Fuel Vehicle (FFV) - The draft final report for this project was submitted to Air Products (no update in this reporting period).

Stationary Turbine for Nitrogen Oxide (NO<sub>x</sub>) Control - The test results on the low-NO<sub>x</sub> gas turbine combustor fueled with stabilized methanol from the LPMEOH™ Demonstration Unit have been prepared. The report on this project should be submitted to Air Products in May of 2000.

West Virginia University (WVU) Stationary Gas Turbine - Testing of stabilized methanol in the gas turbine system has been completed; indications are that the lubrication additive worked well during the final emissions testing. Report preparation is underway; Air Products accepted a request for a 1-½ month no-cost time extension to complete the report. A draft of the paper entitled "Lubricity Problems and Solutions for a Methanol Fueled Gas Turbine" was submitted to the International Mechanical Engineering Conference and Exposition in Orlando, FL (05-10 November 2000).

Aircraft Ground Equipment Emulsion - A final report on the use of a methanol emulsion as the fuel for a flight line generator at Tyndall Air Force Base was sent to Air Products; comments are pending.

University of Florida Fuel Cell - The initial phase of testing of both chemical-grade and stabilized methanol in the second generation methanol steam reforming apparatus has been completed. Both fuels provide similar conversion rates and selectivities; however, the reformat produced with either fuel would be unacceptable for use in fuel cells due to the relatively low methanol conversion rate at the high reformer operating temperature (96% vs. >99% minimum - excess methanol in the reformat will damage the fuel cell). In addition, tests with stabilized methanol showed the presence of oil at the reformer outlet, which would also be unacceptable. A search for a different reformer catalyst is underway, and techniques to filter the oil from the stabilized methanol are being considered.

West Virginia University Tri-Boro Bus - The draft final report for this project was submitted to Air Products (no update in this reporting period).

Florida Institute of Technology Bus & Light Vehicle - The final report on testing of stabilized methanol as a transportation fuel at the Florida Institute of Technology was received. DOE accepted Air Products' recommendation to provide stabilized methanol from the LPMEOH™ Process Demonstration Unit for use as part a new contract between the Institute and the Florida Energy Office. Air Products will receive copies of the reports which are submitted to the State of Florida.

## ***D.2 DME Design Verification Testing***

### Discussion

The first decision milestone, on whether to continue with dimethyl ether (DME) Design Verification Testing (DVT), was targeted for 01 December 1996. This milestone was relaxed to July of 1997 to allow time for further development of the Liquid Phase Dimethyl Ether (LPDME) catalyst system. DVT is required to provide additional data for engineering design and demonstration decision-making. The essential steps required for decision-making are: a) confirm catalyst activity and stability in the laboratory, b) develop engineering data in the laboratory, and c) confirm market(s), including fuels and chemical feedstocks.

Prior work in this task included a recommendation to continue with DME DVT and Market Economic Studies. Ongoing activity is focusing on completing the assessment of the results of the design verification test run at the LaPorte AFDU.

### ***1997 DME DVT Recommendation***

DOE issued a letter dated 31 July 1997 accepting Air Products' recommendation to continue with the design verification testing to coproduce DME with methanol, and to proceed with planning a design verification test run at the LaPorte AFDU. A copy of the recommendation (dated 30 June 1997) is included in Appendix C-1. The recommendation was based on the results of the Market Economic Studies and on the LPDME catalyst system R&D work, and is summarized in the following.

The Market Economic Studies show that the LPDME Process should have a significant economic advantage for the coproduction of DME with methanol for local markets. The studies show that the market applications for DME are large. DME is an ultra clean diesel fuel; and an 80% DME mixture with methanol and water is now being developed and tested by others. DME is a key intermediate in a commercial syngas-to-gasoline process, and is being developed as an intermediate for other chemicals and fuels. An LPDME catalyst system with reasonable long-term activity and stability has been developed from the laboratory R&D work.

Based upon the potential size of the markets and the promise of the LPDME catalyst system, design verification planning for the LaPorte AFDU was recommended. A summary of the DME DVT recommendation is:

- Planning for a DME DVT run at the LaPorte AFDU, in conjunction with other DOE Liquid Fuels Programs, should be initiated. Test plans, budgets, and a schedule for these LaPorte AFDU tests are under development. Up to \$875,000 of Clean Coal Technology Program budget support from the LPMEOH™ Project budget could be made available to support a suitable LPDME test run at LaPorte.
- An implementation decision, made mutually by the DOE's Clean Coal Technology Program (DE-FC22-92PC90543) LPMEOH™ project participants, and by the DOE's Liquid Fuels Program (DE-FC22-95PC93052) project participants, will be made in order to finalize the schedule for testing at LaPorte.

LPDME is not applicable to hydrogen (H<sub>2</sub>)-rich syngas; and it is unlikely that a substantive LPDME demonstration will be recommended for Kingsport. Therefore, a convincing case that the test-run on CO-rich syngas at LaPorte will lead to successful commercialization must be made, prior to approving the final test-run plan. The strategy for commercialization must present the technical logic to combine the results of the following two areas:

- 1) catalyst performance (productivity, selectivity, and life) for the LPDME catalyst system under CO-rich syngas from the design verification testing at the LaPorte AFDU; and
- 2) reactor performance (methanol catalyst activity and life, hydrodynamics, and heat transfer) from the LPMEOH™ Process Demonstration Unit at Kingsport.

The 1997 DME DVT recommendation summarizes the catalyst targets, experimental results, and the corresponding economics for a commercially successful LPDME catalyst.

### ***Market Economic Studies***

Work on the feasibility study for the coproduction of DME and methanol with electric power has been completed. The product DME would be used as a domestic liquid cooking fuel, to replace imported Liquid Petroleum Gas, for China and the Pacific Rim regions. The results are included in the 1997 DME recommendation in Appendix C-1.

### ***Results from Design Verification Testing Activities***

At a review meeting for the DOE's Liquid Fuels Program on 09 June 1999, members of the LPMEOH™ Project Team from Air Products and DOE were given an update on the activities regarding the status of catalyst development and the economics for the LPDME Process. The participants agreed that the next test for the LPDME Process at the LaPorte AFDU should be treated as an interim campaign, with the primary objective being the determination of a tie-point between catalyst performance in the autoclave and the pilot plant scale.

Following this meeting, a formal recommendation to proceed with the interim campaign at the LaPorte AFDU was issued by Air Products to DOE. A copy of this letter (dated 06 August 1999) is included in Appendix C-2. The objectives for this campaign, as stated in this recommendation, were:

- 1) Determine commercial viability of the LPDME Process on a 10 TPD scale, using commercially produced catalysts.
- 2) Obtain information to correlate scale-up of catalyst aging from the laboratory autoclave to the slurry bubble column.
- 3) Conduct process variable testing at conditions of potential commercial interest.
- 4) Perform experiments to better understand the hydrodynamics of the slurry bubble column.

DOE issued a letter dated 10 August 1999 accepting Air Products' recommendation to proceed with DME DVT activities at the LaPorte AFDU.

Execution of the LPDME design verification test at the LaPorte AFDU was completed during October and November of 1999, and preliminary results from the operation were presented in Technical Progress Report No. 22. The major accomplishments of this run are summarized below:

- Commercial viability of the LPDME Process was successfully evaluated on a 10 TPD scale, using commercially produced catalysts. The plant was operated for 25 days to compare catalyst aging in a pilot scale slurry bubble column with that in a laboratory autoclave. The catalyst life study was extended in favor of a planned process variable study to obtain additional data on catalyst aging. Hydrodynamic information was

obtained at the baseline conditions by conducting a detailed survey of the reactor with radioactive tracer injections.

- The deactivation rate for both the catalysts was calculated to be 0.7% per day. This result is lower than the 1.2% per day which had been calculated for both the methanol synthesis and dehydration catalysts during experiments in the autoclave. The rate of deactivation is slightly higher than 0.5% per day rate which was achieved for the LPMEOH™ Process after 3 weeks of operation at LaPorte in 1988/89. The methanol productivity remained relatively constant throughout the run, while the DME productivity showed a slight decline. These trends are consistent with observations from the laboratory. The standard error for the methanol catalyst deactivation rate was high (0.25% per day) due to initial scatter in the data. The scatter decreased significantly after problems in the sampling and analytical system were discovered and resolved at 350 hours on stream. The dehydration catalyst activity data have better statistics, with a standard error of 0.06% per day.
- The 1999 design verification test of the LPDME Process at the LaPorte AFDU represents a significant step forward in the development of the technology. The 0.7% per day rate of catalyst deactivation which was achieved during this campaign is a large improvement over the 4% per day rate of deactivation which was calculated from autoclave studies prior to the initial test of the LPDME Process at the LaPorte AFDU in 1991.

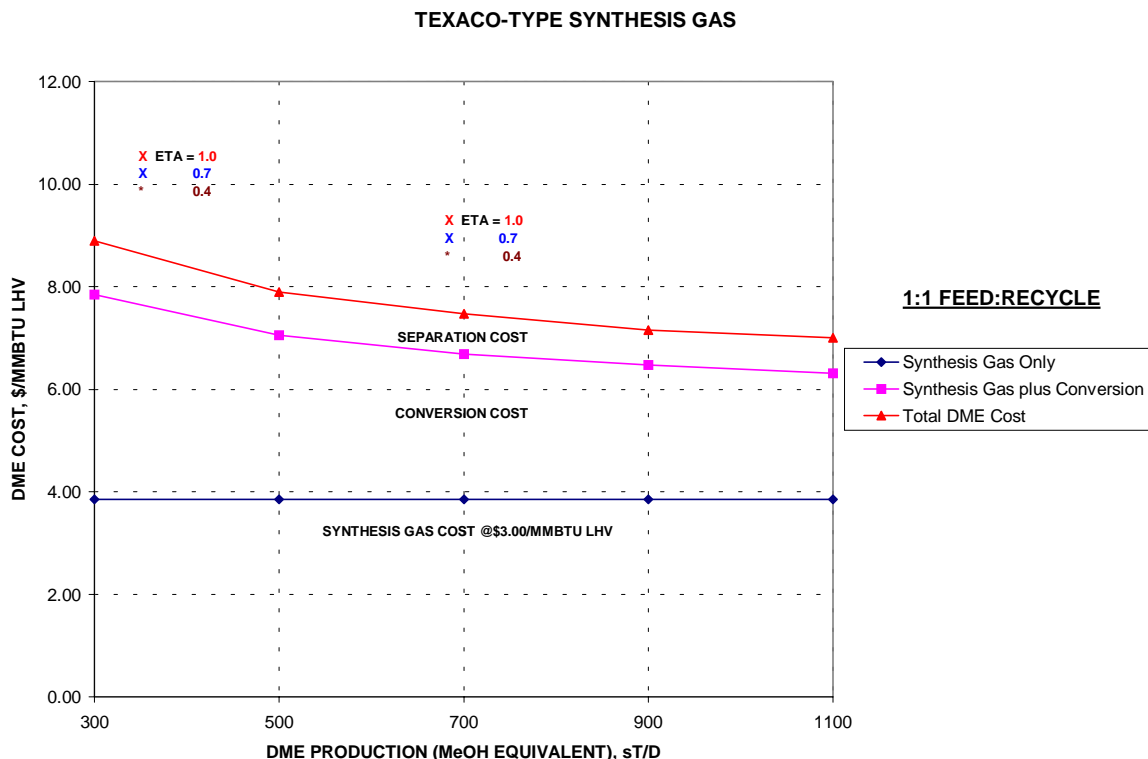
During a Project Review Meeting on 12-13 January 2000, the preliminary results from the LPDME design verification test were presented. A table which compared the performance of the LPDME catalyst system during the Design Verification Test Run with results from the recent work in the laboratory autoclave and the economic targets for the LPDME Process was presented (Table D.2-1). The results from the laboratory work had indicated that the targets for catalyst productivity and life can be met at lower selectivity to DME. The results from the Design Verification Test Run were applied to a cost estimate for a commercial-scale LPDME plant (Figure D.2-1). The case that was considered was the retrofit of an existing Texaco gasifier in China which is currently used in the production of ammonia. The results of this initial work were that, for this syngas (35 vol% H<sub>2</sub>, 51 vol% CO, 13 vol% CO<sub>2</sub>) available at 500 psig, the DME costs are competitive with liquefied petroleum gas (LPG) in China (\$7 - \$8 per million Btu's). The cost of syngas assumes constant utilization for each plant size, and economies of scale are indicated by changes in the conversion and separation costs. The target DME cost can likely be achieved at larger plant sizes by extrapolating the costs to the 1,100 short tons-per-day production rates. The sensitivity of the cost of production of DME to the life of the LPDME catalyst system was shown for the results from LaPorte (0.7% per day deactivation), as well as the impact of changes to the value for catalyst life on the process economics.

As stated in the 30 July 1997 letter which transmitted Air Products' recommendation to proceed with LPDME Design Verification Testing, the basis for commercialization of the technology must come from:

**Table D.2-1**  
**LPDME™ Goals and Performance Results (Laboratory + AFDU)**

	<b>Liquid Fuels Program Goals</b>	<b>Commercial Targets</b>	<b>Laboratory Results (July 1997)</b>	<b>Laboratory Results (June 1999)</b>	<b>AFDU Results (Oct./Nov. 1999)</b>
<b>Catalyst Productivity, mol/kg catalyst-hr (MeOH-equivalent)</b>	> 28 (Initial Productivity)	> 14 (productivity for aged catalyst)	28 (Initial Productivity)	28 (Initial Productivity)	30.5 (Initial Productivity)
<b>Catalyst Selectivity</b>	DME Selectivity > 80% (% Carbon, CO <sub>2</sub> -free)	DME = 75%, Methanol = 25% (heating value basis)	DME Selectivity = 79% (% Carbon, CO <sub>2</sub> -free)	DME Selectivity = 65% (% Carbon, CO <sub>2</sub> -free)	DME Selectivity = 66 (start) - 61 (end)% (% Carbon, CO <sub>2</sub> -free)
<b>Catalyst Life</b>	> 50% Initial Productivity after 1000 hours	Target Productivity after 6 months of operation	57% of Initial Productivity after 1000 hours	61% of Initial Productivity after 1000 hours	Calculated Target Productivity after 3-1/3 months of operation

**Figure D.2-1**  
**LPDME Process Economics**



- 1) the results from testing of the LPDME catalyst system at the LaPorte AFDU; and
- 2) the reactor performance (methanol catalyst activity and life, hydrodynamics, and heat transfer) from the LPMEOH™ Process Demonstration Unit.

After discussing the results from the LPDME Design Verification Testing activities and the ongoing performance results from Kingsport, the meeting participants agreed that the available resources should be directed toward improving the catalyst performance for the LPMEOH™ Process during the remaining time within the operating program. The results of this economic analysis will be forwarded to the DOE's Liquid Fuels Program in order to provide direction to the ongoing catalyst development efforts.

Reporting on the results of the efforts in developing the LPDME Process will be issued as follows:

- 1) Results of the ongoing laboratory program will continue to be published by the DOE's Liquid Fuels Program.
- 2) Results of the Design Verification Test operation at the LaPorte AFDU will be published under the LPMEOH™ Demonstration Project; the expected date for release of the draft topical report is 31 July 2000.

- 3) A market analysis for DME and review of the economics of the LPDME™ Process will be prepared by the LPMEOH™ Demonstration Project following the release of the draft topical report.

### ***D.3 LPMEOH™ Process Demonstration Unit - Methanol Operation***

Table D.3-1 contains the summary table of performance data for the LPMEOH™ Demonstration Unit during the reporting period. These data represent daily averages, typically from a 24-hour material balance period, and those days with less than 12 hours of stable operation are omitted. Appendix D contains samples of the detailed material balance reports which are representative of the operation of the LPMEOH™ Demonstration Unit during the reporting period.

During the reporting period, a total of 5,951,853 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No environmental incidents or injuries were reported during this quarter.

The LPMEOH™ Demonstration Unit experienced two forced outages during the reporting period. The first, which occurred on 17 January 2000 and lasted for 38 hours, was caused by the failure of a localized section of the recirculation piping on a boiler feedwater pump. An analysis of the piping system by Eastman has determined that the root cause of the failure was the proximity of a restricting flow orifice to downstream valving and piping. During the next opportunity, a redesigned section of piping with increased distance from the orifice will be installed; in the interim, inspection of suspect areas of the existing piping system will be performed. Eastman has thoroughly checked other sections of pipe in this area and has found no other problems. This represents the first LPMEOH™ Demonstration Unit forced outage since February 1999.

The second forced outage, which occurred on 22 March 2000, was due to the failure of a control valve which regulates the flowrate of refined methanol from the distillation system. No methanol was emitted as part of this valve failure and there were no environmental or safety incidents. The valve repair was completed on 23 March 2000 and the unit was restarted after about 15 hours of downtime.

As a result of these outages, the availability during the reporting period was 97.52%. Appendix E, Table 1 contains the summary of outages for the LPMEOH™ Demonstration Unit during this quarter.

#### **Catalyst Life ( $\eta$ ) - January - March 2000**

The “age” of the methanol synthesis catalyst can be expressed in terms of a dimensionless variable  $\eta$ , which is defined as the ratio of the rate constant at any time to the rate constant for freshly reduced catalyst (as determined in the laboratory autoclave). Appendix E, Figure 1 plots  $\log \eta$  versus days onstream from the restart in March 1999 to the end of the reporting period. Since catalyst activity typically follows a pattern of exponential decay, the



**Table D.3-1. Data Summary for LPMEOH™ Demonstration Unit**

																		Reactor	Raw		U				
																		O-T-M	Syngas	MeOH	Catalyst	Reactor	Overall	Sparger	Sparger
																		Conv.	Util.	Prod.	MeOH Prod.	Vol. Prod.	(Btu	dP	Resist.
																		(%)	(SCF/lb)	(TPD)	(gmol/hr-kg)	(TPD/ft3)	hr ft2 F)	(psi)	(K")
Case	Date	Stream	Gas Type	Temp (Deg C)	Pres. (psig)	Fresh Feed (KSCFH)	Recycle Gas (KSCFH)	Reactor Feed (H2:CO)	Purge Gas (KSCFH)	Inlet Sup. Velocity (ft/sec)	Space Velocity (l/hr-kg)	Slurry Conc. (wt% ox)	Gas Holdup (vol%)	Gassed Slurry Hgt (ft)	Catalyst Inventory (lb)	Catalyst Age (eta)	CO Conv. (%)	O-T-M Conv. (%)	Syngas Util. (SCF/lb)	MeOH Prod. (TPD)	Catalyst MeOH Prod. (gmol/hr-kg)	Reactor Vol. Prod. (TPD/ft3)	Overall (Btu hr ft2 F)	Sparger dP (psi)	Sparger Resist. (K")
11	1-Jan-00	742	Balanced	235	710	721	1,979	2.91	112.6	0.63	3539	41.5	30.5	54.5	44,924	0.287	30.8	20.8	43.7	198.1	11.50	0.086	163	3.95	4.43
11	2-Jan-00	743	Balanced	235	710	717	1,952	3.05	124.8	0.62	3501	41.4	27.6	52.5	44,924	0.286	31.5	20.5	44.2	194.5	11.31	0.088	165	3.71	4.39
11	3-Jan-00	744	Balanced	235	710	692	1,946	2.93	98.6	0.61	3462	41.4	26.8	52.0	44,924	0.292	31.2	20.8	42.8	193.8	11.26	0.089	163	3.85	4.42
11	4-Jan-00	745	Balanced	235	710	694	1,991	2.82	97.6	0.62	3532	42.6	26.5	49.5	44,924	0.286	29.8	20.6	42.6	195.4	11.35	0.094	179	4.29	4.75
11	5-Jan-00	746	Balanced	235	710	694	2,009	3.06	113.2	0.63	3567	43.0	26.9	49.0	44,924	0.273	29.9	19.6	43.8	190.1	11.03	0.092	172	3.57	4.43
11	6-Jan-00	747	Balanced	235	710	700	1,986	3.25	123.8	0.62	3504	42.5	29.8	52.0	44,924	0.279	31.6	19.8	44.4	189.4	10.99	0.087	169	3.49	4.50
11	7-Jan-00	748	Balanced	235	710	697	1,985	3.02	116.7	0.62	3535	42.9	32.8	53.5	44,924	0.276	29.9	19.8	43.9	190.6	11.07	0.085	160	3.69	4.48
11	8-Jan-00	749	Balanced	235	710	697	2,014	2.82	109.1	0.63	3549	42.9	35.5	55.5	44,924	0.271	28.6	19.9	43.8	191.1	11.09	0.082	153	3.87	4.41
11	9-Jan-00	750	Balanced	235	710	695	2,005	2.65	107.7	0.63	3555	43.3	35.7	55.0	44,924	0.271	27.4	20.0	43.6	191.4	11.10	0.083	152	4.03	4.37
11	10-Jan-00	751	Balanced	235	710	697	1,996	2.65	112.1	0.63	3538	42.9	32.2	53.0	44,924	0.276	27.9	20.1	43.5	192.2	11.16	0.086	157	4.04	4.38
11	11-Jan-00	752	Balanced	235	710	701	2,027	2.79	118.9	0.64	3592	42.9	32.1	53.0	44,924	0.273	28.2	19.7	43.9	191.6	11.13	0.086	154	4.04	4.41
11	12-Jan-00	753	Balanced	235	710	701	1,996	2.71	122.2	0.63	3535	42.5	33.8	55.0	44,924	0.271	27.8	19.7	44.3	189.9	11.03	0.082	149	3.92	4.40
11	13-Jan-00	754	Balanced	235	710	700	2,015	2.63	120.7	0.63	3576	44.2	31.0	49.5	44,924	0.269	26.9	19.5	44.0	190.7	11.08	0.092	165	4.24	4.67
11	14-Jan-00	755	Balanced	235	710	697	2,054	2.68	120.8	0.64	3593	43.2	26.6	48.5	44,924	0.263	26.6	19.2	44.4	188.3	10.93	0.093	165	4.01	4.48
11	20-Jan-00	761	Balanced	235	710	563	2,134	2.42	113.5	0.63	4721	35.9	21.6	45.5	33,687	0.264	19.8	15.2	45.8	147.4	11.41	0.077	164	3.96	4.31
11	21-Jan-00	762	Balanced	235	710	555	2,117	2.43	115.5	0.62	4680	35.7	21.2	45.5	33,687	0.257	19.4	14.9	46.4	143.5	11.11	0.075	144	3.88	4.32
11	22-Jan-00	763	Balanced	234	710	548	2,089	3.13	62.6	0.61	4328	37.3	25.4	48.0	35,887	0.297	27.7	17.5	40.8	161.2	11.71	0.080	135	3.59	4.19
11	24-Jan-00	765	Balanced	234	710	646	2,004	3.95	76.8	0.61	4057	39.0	22.7	46.0	38,087	0.374	38.2	20.4	41.3	187.7	12.85	0.097	162	3.13	4.27
11	3-Feb-00	775	Balanced	235	710	863	1,885	4.21	82.1	0.63	3795	38.7	32.8	56.5	42,487	0.491	44.8	27.4	40.1	258.1	15.83	0.109	157	4.02	4.23
11	4-Feb-00	776	Balanced	235	710	859	1,960	3.29	81.6	0.65	3905	41.3	31.8	53.0	42,487	0.479	43.5	26.5	40.1	256.8	15.75	0.115	167	4.21	4.21
11	5-Feb-00	777	Balanced	235	710	854	1,921	3.27	85.8	0.64	3842	41.0	31.0	53.0	42,487	0.454	42.4	26.1	40.8	251.3	15.41	0.113	157	4.27	3.97
11	6-Feb-00	778	Balanced	235	710	825	1,946	3.31	78.8	0.64	3830	40.8	30.4	53.0	42,487	0.445	42.1	25.6	40.4	245.3	15.04	0.110	147	3.93	4.24
11	7-Feb-00	779	Balanced	234	710	855	1,915	3.16	82.3	0.64	3832	40.8	27.7	51.0	42,487	0.470	42.3	26.5	40.2	255.6	15.68	0.119	160	4.03	4.27
11	8-Feb-00	780	Balanced	234	710	824	1,998	3.27	88.5	0.65	3895	40.8	27.6	51.0	42,487	0.427	40.1	24.8	40.9	241.6	14.82	0.113	150	4.03	4.27
11	9-Feb-00	781	Balanced	234	710	840	1,917	3.29	99.1	0.64	3802	42.7	26.0	46.5	42,487	0.442	41.9	25.7	41.2	244.4	14.99	0.126	169	3.92	4.25
11	10-Feb-00	782	Balanced	234	710	884	1,870	3.14	94.7	0.64	3620	41.7	25.2	50.0	44,687	0.475	43.8	27.5	40.6	261.5	15.25	0.125	152	4.12	4.23
11	11-Feb-00	783	Balanced	233	710	899	1,857	3.10	113.0	0.64	3627	43.1	30.5	51.0	44,687	0.468	42.8	27.3	41.4	260.9	15.19	0.122	140	4.09	4.23
11	12-Feb-00	784	Balanced	233	710	894	1,884	3.11	116.0	0.64	3653	41.4	23.4	49.5	44,687	0.449	41.7	26.7	41.9	256.1	14.93	0.123	139	4.12	4.22
11	13-Feb-00	785	Balanced	233	710	905	1,864	2.96	123.1	0.64	3645	43.2	32.3	52.0	44,687	0.460	41.0	27.1	41.9	259.3	15.14	0.119	132	4.22	4.23
11	14-Feb-00	786	Balanced	233	710	896	1,877	3.02	119.5	0.64	3646	45.6	32.9	48.0	44,687	0.453	41.2	26.8	41.6	258.1	15.06	0.128	147	4.19	4.29
11	15-Feb-00	787	Balanced	235	710	900	1,819	3.48	111.6	0.63	3563	41.7	29.3	53.0	44,687	0.482	47.5	27.9	41.3	261.1	15.23	0.117	159	3.81	4.29
11	16-Feb-00	788	Balanced	235	710	908	1,841	3.39	109.8	0.63	3573	41.2	26.0	51.5	44,687	0.472	46.1	27.5	42.0	259.1	15.12	0.120	159	3.91	4.31
11	17-Feb-00	789	Balanced	235	710	900	1,857	3.12	101.5	0.64	3630	41.3	23.9	50.0	44,687	0.468	43.7	27.6	40.8	264.8	15.45	0.126	168	4.15	4.30
11	18-Feb-00	790	Balanced	235	710	916	1,806	3.29	122.7	0.63	3570	40.9	24.4	51.0	44,687	0.475	45.7	27.9	41.8	262.9	15.29	0.123	166	3.95	4.28
11	19-Feb-00	791	Balanced	235	710	908.7	1,862	3.12	112.2	0.64	3649	42.4	24.9	48.5	44,687	0.467	43.4	24.9	41.2	264.6	15.44	0.130	174	4.30	4.42
25	23-Feb-00	795	Shell	235	710	624	2,237	0.57	85.1	0.66	3760	42.4	35.6	56.5	44,687	0.500	11.4	17.9	42.4	176.6	10.28	0.074	164	8.28	4.19
11	25-Feb-00	797	Balanced	234	700	570	2,041	4.74	26.7	0.61	3423	42.2	22.7	47.5	44,687	0.402	46.3	20.1	38.1	179.2	10.45	0.090	160	3.42	4.17
11	27-Feb-00	799	Balanced	234	710	854	1,949	3.17	129.5	0.65	3689	42.3	26.1	49.5	44,687	0.400	39.3	24.6	43.4	238.4	13.92	0.115	152	4.27	4.21
11	28-Feb-00	800	Balanced	234	710	860	1,956	3.15	135.6	0.65	3726	42.8	26.1	48.5	44,687	0.392	38.5	24.2	43.8	239.3	13.97	0.118	151	4.17	4.19
11	29-Feb-00	801	Balanced	234	710	852	1,942	3.16	133.8	0.65	3689	42.8	26.0	48.5	44,687	0.393	38.8	24.3	43.0	237.9	13.89	0.117	153	4.15	4.22
11	1-Mar-00	802	Balanced	234	710	861	1,944	3.00																	

**Table D.3-1. Data Summary for LPMEOH™ Demonstration Unit (continued)**

Case	Date	Days	Gas	Temp (Deg C)	Pres. (psig)	Fresh	Recycle	Reactor	Purge	Inlet Sup.	Space	Slurry	Gas	Gassed	Catalyst	Catalyst	CO	Reactor		Raw	Catalyst	Reactor	U		Sparger	Sparger
		On				Stream	Type	Feed (KSCFH)	Gas (KSCFH)	Feed (H2:CO)	Gas (KSCFH)	Velocity (ft/sec)	Velocity (l/hr-kg)	Conc. (wt% ox)	Holdup (vol%)	Hgt (ft)	Inventory (lb)	Age (eta)	Conv. (%)	Conv. (%)	Syngas Util. (SCF/lb)	MeOH Prod. (TPD)	MeOH Prod. (gmol/hr-kg)	Vol. Prod. (TPD)(ft3)	Overall (Btu hr ft2 F)	dP (psi)
11	14-Mar-00	815	Balanced	234	710	818	1,966	2.92	130.4	0.65	3674	42.2	26.1	49.5	44,687	0.357	34.9	23.3	43.2	227.4	13.24	0.109	149	4.24	4.24	
11	15-Mar-00	816	Balanced	234	710	835	1,921	2.97	137.0	0.64	3625	42.0	23.8	48.5	44,687	0.374	36.5	23.9	43.4	231.1	13.50	0.114	157	4.08	4.20	
11	17-Mar-00	818	Balanced	234	710	783	2,026	2.91	109.0	0.65	3720	41.6	24.9	50.0	44,687	0.346	33.7	22.6	42.3	222.2	12.96	0.106	148	4.31	4.23	
11	18-Mar-00	819	Balanced	234	710	746	1,997	3.16	131.0	0.64	3635	42.4	23.3	47.5	44,687	0.346	35.8	22.4	41.5	215.5	12.59	0.108	152	3.97	4.16	
11	19-Mar-00	820	Balanced	234	710	808	1,974	2.93	133.6	0.64	3663	41.9	27.2	51.0	44,687	0.353	34.8	23.0	43.5	222.7	13.02	0.104	148	4.22	4.14	
11	20-Mar-00	821	Balanced	234	710	804	1,952	3.03	147.0	0.64	3622	42.4	27.0	50.0	44,687	0.344	35.0	22.7	44.5	216.7	12.66	0.103	147	4.14	4.21	
21	24-Mar-00	825	1:1	235	700	650	2,140	0.95	75.8	0.66	3722	41.0	19.7	48.0	44,687	0.378	15.1	19.1	41.3	189.0	11.04	0.094	167	7.05	4.19	
21	25-Mar-00	826	1:1	235	700	662	2,121	0.93	94.4	0.66	3719	41.4	27.8	52.5	44,687	0.374	14.7	18.8	42.5	186.8	10.92	0.085	152	6.98	4.13	
21	26-Mar-00	827	1:1	235	700	651	2,130	0.94	89.3	0.66	3713	41.4	27.8	52.5	44,687	0.375	14.9	19.0	41.9	186.3	10.89	0.084	150	6.98	4.12	
21	27-Mar-00	828	1:1	234	700	663	2,130	0.96	99.0	0.66	3720	42.2	25.1	49.0	44,687	0.370	15.0	19.1	42.5	187.2	10.94	0.091	158	6.84	4.09	
21	28-Mar-00	829	1:1	234	700	667	2,121	0.97	98.1	0.66	3713	42.5	25.2	48.5	44,687	0.365	15.0	19.0	42.8	187.0	10.93	0.092	149	6.83	4.14	
21	29-Mar-00	830	1:1	234	700	656	2,132	1.05	94.7	0.66	3712	43.2	27.9	49.0	44,687	0.373	16.0	19.5	42.2	186.7	10.91	0.091	150	6.59	3.96	
21	30-Mar-00	831	1:1	234	700	657	2,113	1.08	94.9	0.66	3697	42.7	28.1	50.0	44,687	0.364	16.2	16.2	46.2	186.2	10.88	0.089	143	6.52	4.01	
21	31-Mar-00	832	1:1	234	700	675	2,069	0.96	105.3	0.65	3639	42.2	25.1	49.0	44,687	0.371	15.4	19.3	43.8	185.1	10.82	0.090	111	6.89	4.25	

plot of  $\log \eta$  is fit to a series of straight lines, with step-changes whenever fresh catalyst was added to the reactor.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. A series of four withdrawals were conducted on 19 and 20 January 2000. This was followed by five catalyst additions which were activated and added between 22 January and 10 February 2000. After the addition of the fifth batch of catalyst, the total catalyst inventory was calculated to be 44,687 pounds.

A catalyst activation which was started on 26 January 2000 was aborted due to problems with the composition of the reducing gas. This reduction was initiated with 100 vol% CO instead of the prescribed dilute CO stream (4 vol% CO in N<sub>2</sub>). Changes in the control system and operating procedures have been instituted to prevent the reoccurrence of this event.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.64% per day was calculated for the period 31 December 1999 to 14 January 2000 (15 days). An overall deactivation rate of 0.72% per day was calculated for the period 29 February 2000 to 15 March 2000 (15 days). These deactivation results are greater than the baseline deactivation rate of 0.4% per day from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (this run was performed at 250°C).

During most of the quarter, the flowrate of Balanced Gas was controlled between 680 and 800 KSCFH. During these operating periods, the reactor pressure was set at 710 psig and temperature was maintained at 235°C. Two intervals of CO-rich testing were also performed, and are documented below.

Upon restarting the LPMEOH™ Reactor on 23 February 2000 (after a syngas outage), the composition of the Balanced Gas stream was less than stoichiometric for the production of methanol; this resulted in a reactor inlet H<sub>2</sub>/CO ratio of approximately 0.5. This period of operation on CO-rich syngas lasted about 24 hours.

On 21 March 2000, CO Gas was introduced with the Balanced Gas to achieve a 1:1 H<sub>2</sub>/CO reactor inlet feed composition. Reactor pressure was adjusted to 695 psig during this period of CO Gas addition to allow for proper control of the CO Gas. Approximately 40 KSCFH of CO Gas was introduced with approximately 600 KSCFH of Balanced Gas for this CO-rich feed case. Operation at this condition continued until the forced outage on 22 March 2000. After the restart on 23 March 2000, CO-rich operation resumed; the test at a 1:1 H<sub>2</sub>/CO reactor inlet feed composition was maintained through the end of the reporting period. The catalyst performance met expectations for the quantity of methanol which was produced at these conditions; however, the operating period was not of sufficient length to calculate the rate of catalyst deactivation. This CO-rich condition will be maintained into April of 2000 in order to perform this calculation.

Repairs to two transmitters in the oil addition circuit were made during the period from 11 February to 14 February 2000; during these interruptions, the expanded slurry height reached

a minimum value of less than 50 feet (or 90% of design). The expanded slurry level was increased after completion of repairs on 15 February 2000. No impact to the system hydrodynamics or operation was observed.

During the reporting period, analyses of catalyst and gas samples for changes in physical characteristics and levels of poisons have continued. Appendix E, Table 2 summarizes the results to date. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. As reported in Technical Progress Report No. 21, the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Unit and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas were changed in June of 1999; the 10C-30 was charged with arsine-removal adsorbent, and the 29C-40 was split between arsine and carbonyl removal materials. Initial results of batch sampling of the Balanced Gas stream demonstrated that the guard-bed system was effective in removing arsenic when it first came on-stream after the changeout. However, subsequent analysis confirmed that arsenic had broken through the guard-bed system within 2 to 3 months of initial operation. Although there is scatter in the data, the results of analyses of catalyst samples confirm this conclusion. The most recent concentration of arsenic on the methanol synthesis catalyst is 1,250 ppmw. In addition, sulfur (another known catalyst poison) is present at about 400 ppmw, and is increasing slowly with time. Work is continuing to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur from the Balanced Gas. The concentration of iron, although low (about 200 ppmw), is increasing in the most recent samples.

#### In-situ Catalyst Activation

Process simulation work was performed in order to determine the operating procedures which could be used during a potential test of in-situ catalyst activation within the LPMEOH™ Reactor. A protocol for testing the potential in-situ catalyst activation conditions in the laboratory autoclave was developed and formalized. Preliminary laboratory testing has begun and will continue into April of 2000 to fully evaluate the procedure.

#### Sparger Resistance

The performance of the gas sparger continues to meet the design expectations for pressure drop and reactor operation. Appendix E, Figure 2 plots the average daily sparger resistance coefficient for the period following the March 1999 outage. The data for this plot, along with the corresponding average pressure drop, are also included in Table D.3-1. The flow resistance will be monitored in order to determine the changes in performance with operating time.

#### ***D.4 Planning and Administration***

A Project Review Meeting was held in Kingsport, TN, on 12-13 January 2000. The results of the unit operation were reviewed, and the preliminary results from the Fall 1999 operating campaign for the LPDME Process at the LaPorte AFDU were presented. The meeting agenda, extracts from the meeting handouts, and the meeting notes are included in Appendix F.

The Milestone Schedule Status Report and the Cost Management Report, through the period ending 31 March 2000, are included in Appendix G. These two reports show the current schedule, the percentage completion and the latest cost forecast for each of the Work Breakdown Structure (WBS) tasks. Ninety-nine percent (99%) of the \$38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 March 2000. Fifty-five percent (55%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2000.

The monthly reports for January, February, and March were submitted. These reports include the Milestone Schedule Status Report, the Project Summary Report, and the Cost Management Report.

A formal request was made to DOE to approve a no-cost time extension to 31 March 2003 for the LPMEOH™ Demonstration Project. This extension is necessary to complete some of the key tests which were originally defined in the September 1996 Demonstration Test Plan, and to allow the opportunity to perform new tests of significant commercial interest (such as in-situ catalyst activation). Supporting information, including a project summary and chronology of events, was also prepared.

An abstract and paper entitled “Liquid Phase Methanol (LPMEOH™) Process Development” was accepted for presentation at Energex 2000 - The 8<sup>th</sup> International Energy Forum (23-28 July 2000). An abstract for the paper entitled “Catalyst and Process Development for Liquid Phase DME Synthesis” was submitted. This paper will be presented at 17<sup>th</sup> Annual International Pittsburgh Coal Conference (11-15 September 2000).

A proposed modification to the Environmental Monitoring Plan (EMP), which dealt with changes to the types of reports which will be produced by the Partnership, was approved by DOE. Those pages which were impacted by this modification were issued for inclusion into the EMP.

Volume 1 - Public Design, of the Final Report for the LPMEOH™ Demonstration Project was issued during the reporting period.

## **E. Planned Activities for the Next Quarter**

- Continue to analyze catalyst slurry samples and reactor performance data to determine causes for deactivation of methanol synthesis catalyst.
- Continue executing Phase 3, Task 2.1 Methanol Operation per the Demonstration Test Plan. Focus activities on increasing catalyst activity, monitoring the performance of the gas sparger in the reactor, and developing the procedure for in-situ catalyst activation.
- Identify new adsorbent materials for use in the 29C-40 guard bed within the LPMEOH™ Demonstration Unit to increase the removal efficiency of arsine and sulfur. Complete assessment of changes in levels of iron on catalyst samples.
- Secure the 15-month, no-cost time extension to the Cooperative Agreement from DOE.
- Issue the draft Topical Report on the Fall 1999 LPDME design verification test at the LaPorte AFDU.
- Continue execution of the Off-Site, Product-Use Test Program (Phase 1, Task 1.4).
- Conduct a Project Review Meeting with DOE.

## **F. Conclusion**

During the reporting period, the availability of the LPMEOH™ Demonstration Unit was 97.52%. A forced outage on 17 January 2000 lasted for 38 hours, and was caused by the failure of a localized section of the recirculation piping on a boiler feedwater pump. During the next opportunity, a redesigned section of piping with increased distance from the orifice will be installed; in the interim, inspection of suspect areas of the existing piping system will be performed. This represents the first LPMEOH™ Demonstration Unit forced outage since February 1999.

The second forced outage, which occurred on 22 March 2000, was due to the failure of a control valve which regulates the flowrate of refined methanol from the distillation system. The plant was restarted after about 15 hours of downtime.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. A series of four withdrawals were conducted on 19 and 20 January 2000. This was followed by five catalyst additions which were activated and added between 22 January and 10 February 2000. After the addition of the fifth batch of catalyst, the total catalyst inventory was calculated to be 44,687 pounds.

A catalyst activation which was started on 26 January 2000 was aborted due to problems with the composition of the reducing gas. This reduction was initiated with 100 vol% CO instead of the prescribed dilute CO stream (4 vol% CO in N<sub>2</sub>). Changes in the control

system and operating procedures have been instituted to prevent the reoccurrence of this event.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.64% per day was calculated for the period 31 December 1999 to 14 January 2000 (15 days). An overall deactivation rate of 0.72% per day was calculated for the period 29 February 2000 to 15 March 2000 (15 days). These deactivation results are greater than the baseline deactivation rate of 0.4% per day from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (this run was performed at 250°C).

During most of the quarter, the flowrate of Balanced Gas was controlled between 680 and 800 KSCFH. During these operating periods, the reactor pressure was set at 710 psig and temperature was maintained at 235°C.

Two intervals of testing on CO-rich syngas were performed during the quarter. Upon restarting the LPMEOH™ Reactor on 23 February 2000 (after a syngas outage), the composition of the Balanced Gas stream was less than stoichiometric for the production of methanol; this resulted in a reactor inlet H<sub>2</sub>/CO ratio of approximately 0.5. This period of operation on CO-rich syngas lasted about 24 hours.

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Process simulation work was performed in order to determine the operating procedures which could be used during a potential test of in-situ catalyst activation within the LPMEOH™ Reactor. A protocol for testing the potential in-situ catalyst activation conditions in the laboratory autoclave was developed and formalized. Preliminary laboratory testing has begun and will continue into April of 2000 to fully evaluate the procedure.

Analyses of catalyst samples for changes in physical characteristics and levels of poisons have continued. Copper crystallite size measurements have shown an increase over time,

which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. Levels of arsenic are continuing to increase on catalyst samples, which confirms earlier observations that the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Plant and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas are no longer effective. Work is continuing to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur (another known catalyst poison) from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is continuing to increase in the most recent samples.

The performance of the gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The performance to date has met the design expectations for pressure drop and reactor operation.

During the reporting period, a total of 5,951,853 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 53.5 million gallons of methanol has been produced. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No safety or environmental incidents were reported during this quarter.

During this quarter, planning, procurement, and test operations continued on two project sites selected for the off-site, product-use test program. Testing of stabilized methanol in the stationary gas turbine system at West Virginia University has been completed; indications are that the lubrication additive worked well during the final emissions testing. Report preparation is underway; Air Products accepted a request for a 1-½ month no-cost time extension to complete the report. A draft of the paper entitled "Lubricity Problems and Solutions for a Methanol Fueled Gas Turbine" was submitted to the International Mechanical Engineering Conference and Exposition in Orlando, FL (05-10 November 2000). The initial phase of testing of both chemical-grade and stabilized methanol in the second generation methanol steam reforming apparatus at the University of Florida has been completed. Both fuels provide similar conversion rates and selectivities; however, the reformat produced with either fuel would be unacceptable for use in fuel cells due to the relatively low methanol conversion rate at the high reformer operating temperature (96% vs. >99% minimum - excess methanol in the reformat will damage the fuel cell). In addition, tests with stabilized methanol showed the presence of oil at the reformer outlet, which would also be unacceptable. A search for a different reformer catalyst is underway, and techniques to filter the oil from the stabilized methanol are being considered.

During a Project Review Meeting on 12-13 January 2000, the preliminary results from the Fall 1999 design verification test of the LPDME Process at the LaPorte AFDDU were presented. The earlier results from the laboratory work had indicated that the targets for catalyst productivity and life can be met at lower selectivity to DME. The results from the Design Verification Test Run were applied to a cost estimate for a commercial-scale LPDME plant. The target DME cost (\$7 to \$8 per million Btu's) can likely be achieved at larger plant sizes by extrapolating the costs to the 1,100 short tons-per-day production rates.



The sensitivity of the cost of production of DME to the life of the LPDME catalyst system was shown for the results from LaPorte (0.7% per day deactivation), as well as the impact of changes to the value for catalyst life on the process economics.

After discussing the results from the LPDME Design Verification Testing activities and the ongoing performance results from Kingsport, the meeting participants agreed that the available resources should be directed toward improving the catalyst performance for the LPMEOH™ Process during the remaining time within the operating program. The results of this economic analysis will be forwarded to the DOE's Liquid Fuels Program in order to provide direction to the ongoing catalyst development efforts.

Work began to prepare the draft Topical Report on the results of the Design Verification Test operation at the LaPorte AFDU; this report, which will be published under the LPMEOH™ Demonstration Project; is expected to be released by 31 July 2000.

A formal request was made to DOE to approve a no-cost time extension to 31 March 2003 for the LPMEOH™ Demonstration Project. This extension is necessary to complete some of the key tests which were originally defined in the September 1996 Demonstration Test Plan, and to allow the opportunity to perform new tests of significant commercial interest (such as in-situ catalyst activation). Supporting information, including a project summary and chronology of events, was also prepared.

An abstract and paper entitled "Liquid Phase Methanol (LPMEOH™) Process Development" was accepted for presentation at Energex 2000 - The 8<sup>th</sup> International Energy Forum (23-28 July 2000). An abstract for the paper entitled "Catalyst and Process Development for Liquid Phase DME Synthesis" was submitted. This paper will be presented at 17<sup>th</sup> Annual International Pittsburgh Coal Conference (11-15 September 2000).

A proposed modification to the Environmental Monitoring Plan, which dealt with changes to the types of reports which will be produced by the Partnership, was approved by DOE.

Volume 1 - Public Design, of the Final Report for the LPMEOH™ Demonstration Project was issued during the reporting period.

Ninety-nine percent (99%) of the \$38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 March 2000. Fifty-five percent (55%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2000.

## **APPENDICES**

### **APPENDIX A - SIMPLIFIED PROCESS FLOW DIAGRAM**

## **APPENDIX B - OFF-SITE TESTING (DEFINITION AND DESIGN)**

### **Appendix B-1 - Summary Table of Seven Test Sites**

#### **Quarterly Reports:**

**Appendix B-2 - University of Florida Fuel Cell (seven pages)**

**Appendix B-3 - Florida Institute of Technology (twenty-nine pages)**

## **APPENDIX C - DME DESIGN VERIFICATION TESTING**

**Appendix C-1 - 1997 DME Design Verification Testing Recommendation  
(fourteen pages)**

**Appendix C-2 - Recommendation to Proceed with Fall 1999 Test at LaPorte AFDU  
(nine pages)**

## **APPENDIX D - SAMPLES OF DETAILED MATERIAL BALANCE REPORTS**

## **APPENDIX E - RESULTS OF DEMONSTRATION UNIT OPERATION**

**Table 1 - Summary of LPMEOH<sup>TM</sup> Demonstration Unit Outages -  
October/December 1999**

**Table 2 - Summary of Catalyst Samples - Second Catalyst Batch**

**Figure 1 - Catalyst Age ( $\eta$ ): August - December 1999**

**Figure 2 - Sparger Resistance Coefficient vs. Days Onstream  
(August 1999 - December 1999)**

**Table 1**  
**Summary of LPMEOH™ Demonstration Unit Outages - January/March 2000**

Operation Start	Operation End	Operating Hours	Shutdown Hours	Reason for Shutdown
1/1/00 00:00	1/17/00 14:30	398.5	38.0	BFW Piping Failure
1/19/00 04:30	2/21/00 07:30	795.0	41.0	Syngas Outage
2/23/00 00:30	3/16/00 12:13	539.7	12.3	Syngas Outage
3/17/00 00:30	3/22/00 12:12	131.7	14.8	Refined MEOH Valve Failure
3/23/00 03:00	3/31/00 23:59	213.0		End of Reporting Period
Total Operating Hours			2077.9	
Syngas Available Hours			2130.7	
<b>Plant Availability, %</b>			<b>97.52</b>	

**Table 2**  
**Summary of Catalyst Samples - Second Catalyst Batch**

Sample	Identity	XRD		BET	Analytical (ppmw)				
		Cu	ZnO	m2/g	Fe	Ni	S	As	Cl
K9804-1	Reduction Sample 4/2/98 - Alternative Catalyst	72.5	84.9	105	23	11	<=110	<=12	
K9712-1	Transfer sample from 29D-02 to Reactor	95.3	74		362	47.2	66.7	10.2	nd
K9712-2	Reactor Sample Day 1	100	123.8	75	92.1	<=18	<=167	<50	nd
K9712-3	Reactor Sample Day 4	130.9	64						
K9712-4	Reactor Sample Day 10	126.8	73.3	73	126	<=22	<=127	<50	nd
K9801-2	Reactor Sample 1/26/98	132.05	98.3		63.5	39.5	42.7	29.2	<100
K9802-1	Reactor Sample 2/3/98	141.1	91.5						
K9802-2	Reactor Sample 2/9/98	158.1	113						
K9802-3	Reactor Sample 2/15/98	145.7	91		67.1	36	<=97	209	
K9802-4	Reactor Sample 2/23/98	176.8	114.5						
K9803-2	Reactor Sample 3/10/1998	154.3	95.8	44	61.4	35.8	<=94	408	
K9803-4	Reactor Sample 3/29/98	169.6	87.9						
K9804-2	Reactor Sample 4/14/98	152.4	89.3		81.7	30.8	<=170	615	
K9805-2	Reactor Sample 5/11/98	219.2	109.6		73.15	35.85	163	538	
K9606-2	Reactor Sample 6/16/98	272.3	117.2		86.4	31.1	220	1110	
K9807-2	Reactor Sample 7/8/98	263.2	108.6		88.7	27.6	277	1045	
K9807-3	Reactor Sample 7/29/98	412*	112		93.25	30.95	209	1620	
K9807-4	Reactor Sample 8/14/98	353.9*	124		121.5	37.1	213.5	1215	
K9809-1	Reactor Sample 9/24/98	347.4	129.8		69.6	29.8	326	1149	
K9810-1	Reactor Sample 10/5/98	331.1	130.4						
K9811-2	Reactor Sample 11/25/98	293.9			57.3	23.4	264	1400	<100
K9812-1	Reactor Sample 12/29/98	283.1			72.3	20.4	260	1300	<100
K9901-1	Reactor Sample 1/15/99	252.5	61.4						
K9902-1	Reactor Sample 2/17/99	474.7	133.6		82.6	22.2	385	1490	<300
K9904-3	Reactor Sample 4/27/99	417.8	110.4	15	131	18.2	348	1460	<30
K9906-1	Reactor Sample 6/1/99	517	105	43	109	19.7	316	1680	40
K9907-1	Reactor Sample 7/13/99	446	116	59	175	19.7	488	1810	30
K9908-2	Reactor Sample 8/31/99	632	117	56	161	15.1	406	1470	50
K9909-2	Reactor Sample 9/21/99	357	109	64	132	11.2	253	1050	nd
K9910-2	Reactor Sample 10/19/99	135	94	55	157	15.4	343	1270	30
K9911-1	Reactor Sample 11/4/99				184	12.8	335	1580	na
K9912-1	Reactor Sample 12/8/99	797	121	60	167	13.9	248	1400	40
K0001-1	Reactor Sample 1/5/00	613	105	63	199	10.8	292	1190	nd
K0001-2	Reactor Sample 1/19/00				205	10.0	432	1250	na

Notes:

- 1) nd = none detected
- 2) \* - these values represent re-analysis of the sample as compared to Technical Progress Report no. 17
- 3) na = data not available



Figure 1

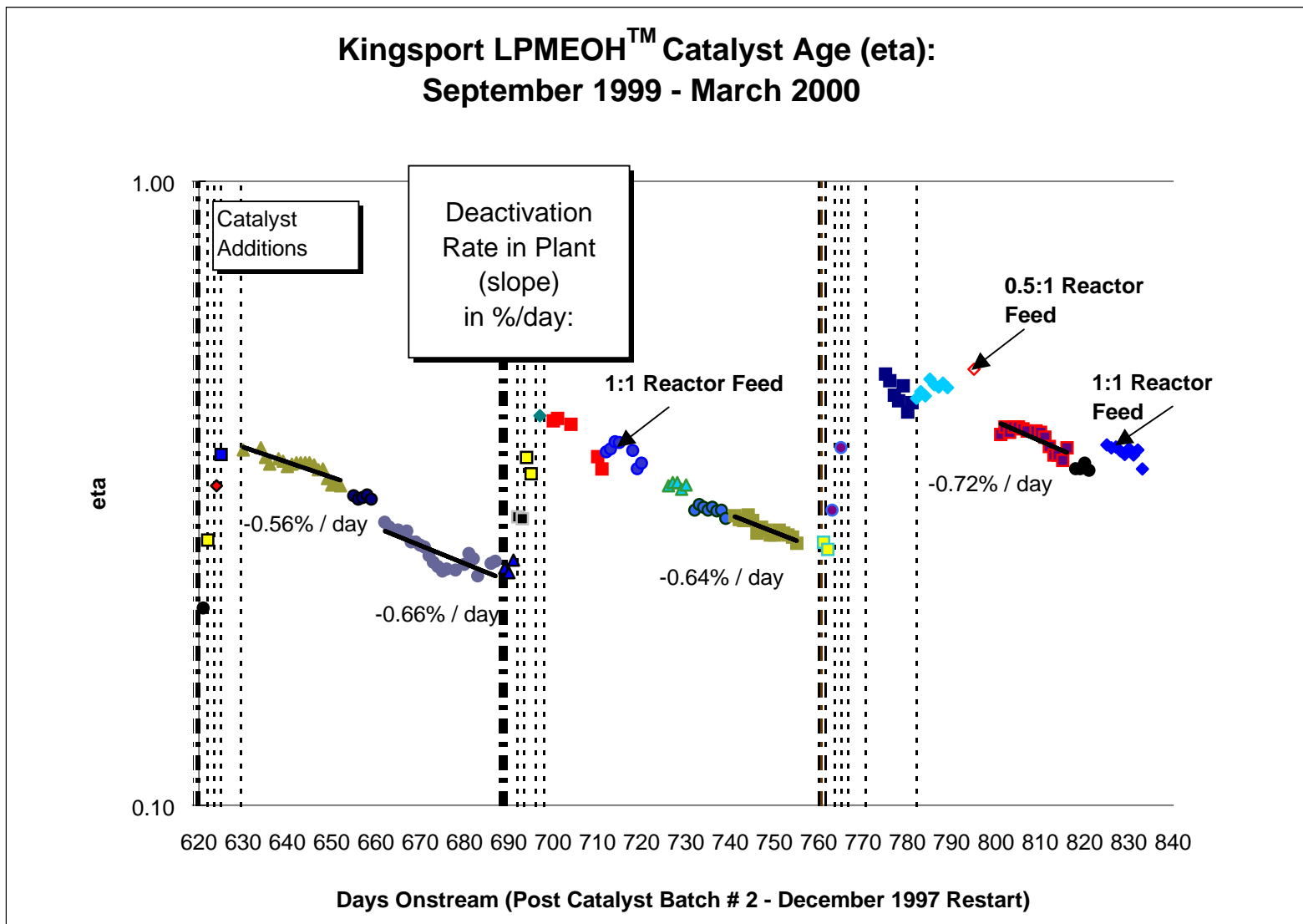
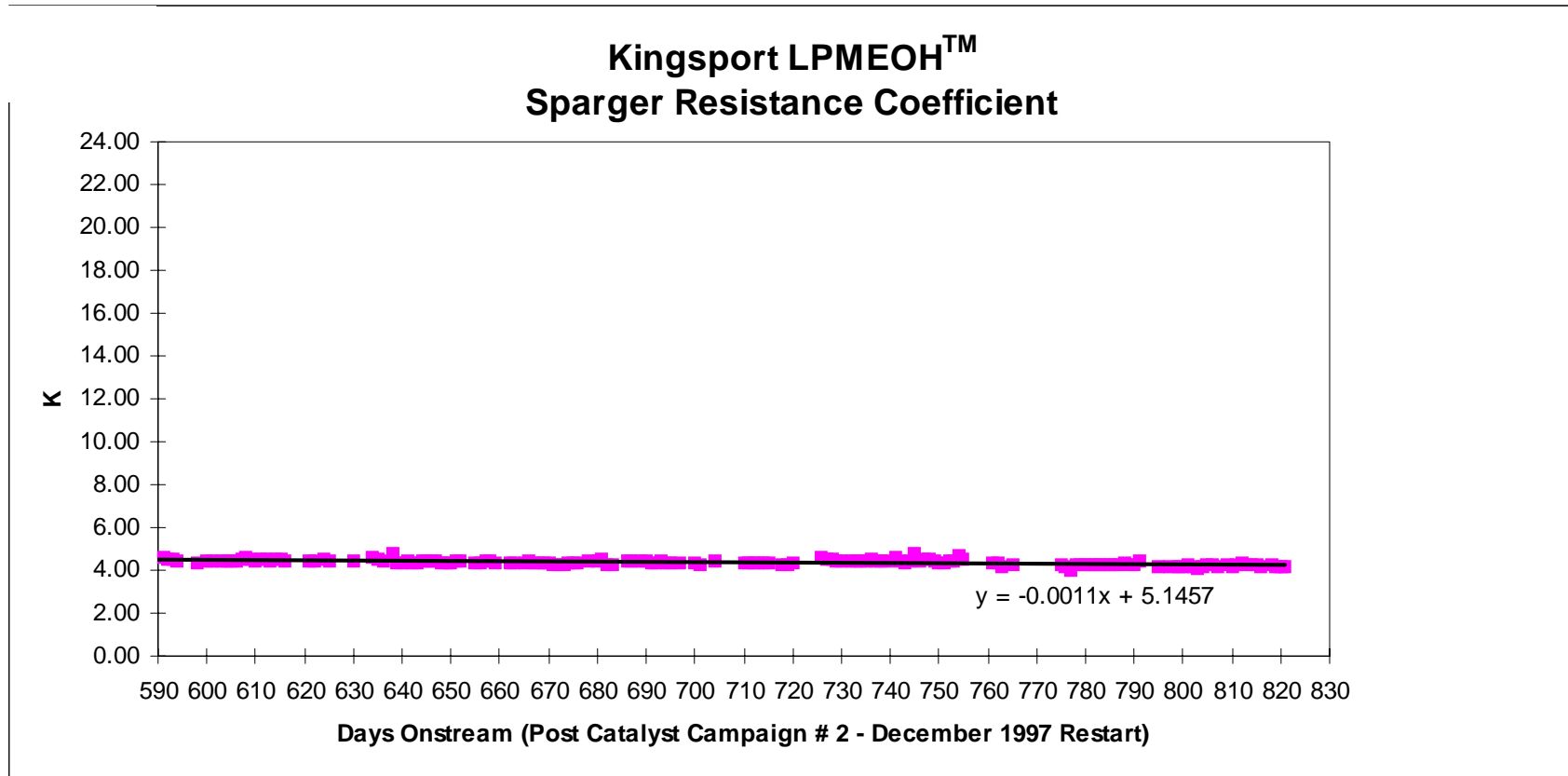


Figure 2



## **APPENDIX F - PROJECT REVIEW MEETING (12-13 JANUARY 2000)**

**APPENDIX G - MILESTONE SCHEDULE STATUS AND COST MANAGEMENT  
REPORTS**